Reciprocity Theorems for Ab Initio Force Calculations

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We present a method for calculating *ab initio* interatomic forces which scales quadratically with the size of the system and provides a physically transparent representation of the force in terms of the spatial variation of the electronic charge density. The method is based on a reciprocity theorem for evaluating an effective potential acting on a charged ion in the core of each atom. We illustrate the method with calculations for diatomic molecules.

Presently, first-principles computational methods can be used to study the equilibrium ground-state structures and transient excited-state relaxation pathways even for relatively complex systems containing as many as several hundred atoms [1]. In these calculations one is guided through a large phase space of possible atomic configurations by following the gradients with respect to the classical nuclear coordinates of the total energy of a system of interacting electrons and ions. On the Born-Oppenheimer ground-state surface these gradients can be obtained by exploiting a force theorem (the Hellmann-Feynman theorem) [2] which states that for any linear variation of a control parameter λ in the quantum mechanical Hamiltonian

$$\frac{\partial U}{\partial \lambda} = \left\langle \frac{\partial H}{\partial \lambda} \right\rangle \tag{1}$$

where U is the total energy of the system, H is the Hamiltonian and the brackets denote an expectation value in the electronic ground state. Using the control parameter λ to denote the nuclear coordinate $R_{I\alpha}$ the theorem immediately provides the force acting on the I-th lattice site with the α-th polarization.

In this paper we discuss a reciprocity theorem which provides a particularly efficient scheme for evaluating the forces in equation (1). One often regards (1) as measuring a response of the quantum electronic charge distribution to an ionic displacement, and indeed the expectation value requires an average of a nuclear deformation potential in the electronic ground state. Alternatively, the left hand side of equation (1) is a force on a classical ion responding to the total electric field seen at the ion site. One can exploit this latter point of view to greatly simplify the calculation and interpretation of this force. We present a reciprocity theorem for inverting this problem which applies even in the general case where the interaction between the electronic and nuclear degrees of freedom is described by effective potentials [1]. Using this theorem the evaluation of (1) for a system containing N_a atoms scales [3] as N_a^2 rather than as N_a^3 as in current electronic structure calculations [1]. The method also greatly aids the interpretation of these forces by directly relating them to the spatial distribution of the ground-state charge density.

Our starting point is a Hamiltonian [4] describing an interacting system of ions and electrons, with the ionic degrees of freedom treated classically, $H = H_k + H_{ee} + H_{\text{ion}-\text{ion}} + H_{\text{el}-\text{ion}}$:

$$H = \sum_i -\frac{\hbar^2}{2m}\nabla_i^2 + \frac{1}{2}\sum_{i \neq j}\frac{e^2}{|r_i - r_j|}$$
$$+ \frac{1}{2}\sum_{I \neq J}\frac{Z_I Z_J e^2}{|R_I - R_J|} + V_{\text{el}-\text{ion}} \tag{2}$$

The potential $V_{\text{el}-\text{ion}}$ may be either a Coulomb potential or a more sophisticated effective potential for treating only the valence electronic degrees of freedom. In either case the Hamiltonian for the system depends parametrically on the ionic coordinates R_I only through the last two terms on the right hand side of equation (2) so that by using the force theorem, one has:

$$F_{I\alpha} = -\nabla_{R_{I\alpha}}U = -\frac{\partial H_{\text{ion}-\text{ion}}}{\partial R_{I\alpha}} - \left\langle \frac{\partial V_{\text{el}-\text{ion}}}{R_{I\alpha}} \right\rangle \tag{3}$$

If we assume that the electrons and ions interact through the simple Coulomb potential, then one can rewrite equation (3) from the point of view of the classical ions by first isolating the part of the total energy which depends on the nuclear coordinates:

$$\frac{1}{2}\int \rho_{\text{ion}}(r)V_{\text{ion}}(r)d^3r + \int \rho_{\text{el}}(r)V_{\text{ion}}(r)d^3r \tag{4}$$

where ρ_{el} is the electronic charge density, $\rho_{\text{ion}}(r) = \sum_I Z_I e\delta(r - R_I)$ denotes the ionic charge density, and $V_{\text{ion}}(r)$ is the electrostatic potential produced by the ionic source distribution ρ_{ion}. The second term can be rewritten by observing that the electronic Hartree potential satisfies $-\frac{1}{4\pi}\nabla^2 V_H = \rho_{\text{el}}(r)$, so that after integrating twice by parts, one has

$$U_{\text{el}-\text{ion}} = \int V_H(r)(-\frac{1}{4\pi}\nabla^2 V_{\text{ion}}(r))d^3r \tag{5}$$

For a system of point ions, the second factor in the integrand is $\sum_I Z_I e\delta(r - R_I)$. Thus differentiation with respect to the ionic coordinates explicitly shows that the force on each ion is a response to the electric field, $-\nabla V_H(r)$ acting at the ionic site as one expects.

The first term in expression (4) also contributes to the electric field acting on the I-th site through the gradient $-\nabla \sum_{J \neq I} V_{\rm ion}(r - R_J)$ i.e. the gradient of the potential produced by the unscreened ions excluding the contribution from the I-th site. Combining these two contributions for the I-th ion, one has

$$V_I(r) = \sum_{J \neq I} V_{\rm ion}(r - R_J) + V_H(r) \qquad (6)$$

so that $F_{I\alpha} = -Z_i e\nabla_{I\alpha} V_I$

The restriction on the sum in equation (6) represents an awkward computational constraint since in principle the sum is different for each ionic site in the system. However, this can be dealt with efficiently by redistributing each ionic point charge uniformly on a spherical shell at some desired atomic sphere radius, a_c in the first term of (6). This shell provides a potential V_s which has the correct $1/r$ dependence for $r > a_c$ and is constant for $r < a_c$, so that the spatially varying part of V_s near the i-th site correctly represents the constrained sum in (6). With this replacement the effective potential V_I which governs relaxation of the classical ions can be obtained for all the lattice sites I in a single calculation.

We illustrate the method with a calculation on the diatomic molecule H_2. In figure 1 we present a map of the equipotentials of equation (6) within an atomic sphere centered around one of the H ions in the molecule. The three panels give the equipotentials calculated using the local density approximation (LDA) to the exchange and correlation energies, for three different interatomic separations. In all cases a minimum in this potential lies near the center of the atomic sphere. For the compressed H_2 the minimum lies at larger separation, and for the expanded molecule at a smaller separation. The force, calculated from the gradient of this potential, is plotted as a function of interatomic separation in figure 2, where we overlay the forces obtained by direct use of the force theorem (1), and as expected the two agree exactly. The inner panel gives the offset between the interatomic separation and the separation which minimizes the effective potential computed for each separation. This shows quite accurately the equilibration of the molecule at the LDA bond length of 0.78A.

The essence of the force theorem is that to lowest order in the nuclear displacements, the electronic charge density can be regarded as rigid. In (1) one then performs an average of the deformation potential in this rigid density. In (5) we use this rigid charge density as a source term in the Poisson equation to extract the effective potential near the ionic site. The equivalence between these two reciprocal points of view applies to all types of interatomic interactions, including metallic, covalent, and even van der Waals bonding, as long as an accurate representation of the charge density is in hand.

This method can be generalized to a system of electrons and ions interacting through any local pseudopotential $V_{\rm ps}(r)$. A pseudopotential generally does not retain the $1/r$ singularity as r $\to$ 0, and thus the partial integrations leading to (5) no longer project the Hartree potential exactly onto a lattice site. However, by replacing $V_{\rm ion}$ by $V_{\rm ps}$ in (5) one sees that the interaction energy can always be obtained by integrating the Hartree potential over an effective ionic charge density which is calculated by taking the Laplacian of $V_{\rm ps}$. Alternatively we observe that the interaction energy $U_{\rm ps}$ has the form:

$$U_{\rm el-ion} = \sum_I \int \rho_{\rm el}(r) V_{\rm ps}(r - r')\delta(r' - R_I)d^3r d^3r' \quad (7)$$

so that by integrating over the coordinate r *first,* one has

$$U_{\rm el-ion} = \sum_I \int V_{\rm eff}(r') Z_I e\delta(r' - R_I)d^3r' \qquad (8)$$

Equation (8) explicitly shows that after the spatial average, a point nucleus experiences an effective potential where $\rho_{\rm el}$ is the source term, and for which the interaction kernel is the effective pseudopotential. If the pseudopotential is replaced by the bare Coulomb potential, the effective potential acting on a lattice site is just the electronic Hartree potential as we found earlier.

In figure 3 we apply this method to molecular H_2, but now calculated replacing the H ions by pseudo-ions. In the main part of the figure we overlay the forces calculated from the force theorem and calculated using the reciprocity relation, and again the two agree exactly. The inset gives the distance from the center of the sphere to the potential minimum as a function of interatomic separation, and confirms that this offset crosses zero at the expected equilibrium separation.

Accurate first-principles pseudopotentials frequently require a nonlocal representation $V_{\rm ps}(r, r')$, so that the interaction energy analogous to equation (7) has the form:

$$U_{\rm el-ion} = \sum_{n,I} \int \psi_n^*(r) V_{\rm ps}(r - R_I, r' - R_I)$$
$$\psi_n(r')d^3r d^3r' \qquad (9)$$

and the sum is over occupied single-particle states ψ_n. Thus the interaction energy involves an integral over the full one-particle density matrix $\rho(r, r')$ rather than simply the charge density alone, i.e.

$$U_{\rm el-ion} = {\rm Tr}\rho(r, r') V_{\rm ps}(r, r') \qquad (10)$$

Inverting this relation along the lines of equations (5) and (7) requires the solution of a generalized Poisson equation with a source term which is the one-particle density matrix. Instead, by integrating equation (9) over a single intermediate coordinate s we obtain

2

$$U_{\text{el-ion}} = \sum_{n,I} \int \psi_n^*(r) V_{\text{ps}}(r-s, r'-s) \psi_n(r')$$

$$d^3r d^3r' \delta(s-R_I) d^3s$$

$$= \sum_I \int V_{\text{eff}}(s) Z_I e \delta(s-R_I) d^3s \quad (11)$$

with

$$V_{\text{eff}}(s) = \frac{1}{Z_I e} \int \rho(r,r') V_{\text{ps}}(r-s, r'-s) d^3r d^3r' \quad (12)$$

This potential simplifies still further if the effective nonlocal potential is expressed as a sum of separable potentials as in Kleinman and Bylander's construction [5]

$$V_{\text{el-ion}}(r,r') = \sum_{I,c} \phi_c(r-R_I) \alpha_c \phi_c^*(r'-R_I) \quad (13)$$

where the $\phi_c(r-R_I)$ are a set of projection functions centered on the I-th ionic site, and α_c are the associated weights. Expressing the one-electron states with the Fourier expansion

$$\psi_{nk}(r) = \sum_G e^{i(k+G)\cdot r} c_{nk}(G) \quad (14)$$

the nonlocal contribution to the interaction energy is

$$U_{\text{el-ion}} = \sum_{GG'} \sum_{nk} \sum_{I,c} e^{-i(G-G')\cdot R_I}$$

$$\langle k+G|\phi_c\rangle \alpha_c \langle \phi_c|k+G'\rangle c_{nk}^*(G) c_{nk}(G') \quad (15)$$

In equation (15) the electronic ground state enters through the density matrix elements $\sum_{nk} c_{nk}^*(G) c_{nk}(G')$, while the plane-wave matrix elements of the nonlocal potential appearing in the sum are normally tabulated in an atomic pseudopotential code. Thus the generalized kernel which connects the one-particle density matrix to the nuclear coordinate is the nonlocal potential.

As an illustration of the method we have applied the prescription in equation (15) to the Cl_2 dimer. Here the Cl ions are represented by nonlocal pseudopotentials [6] in the Kleinman-Bylander form. In figure (4) we display the force on each ion as a function of the interatomic separation, overlaying the forces computed from the Hellmann-Feynman force theorem and from the reciprocity relation. As expected, the two agree exactly, confirming the validity of the construction.

For a system containing N_a sites, the evaluation of $U_{\text{el-ion}}$ (and its gradients) using the reciprocity theorem scales [7] as $N_a^2 \log_2 N_a$ rather than as N_a^3 as would be required for a direct evaluation of equation (15). This occurs because the Kleinman-Bylander projection functions $\phi_c(r-R_I)$ for different atoms I, but the same atom type, differ only in the location of the guiding centers, R_I. Then one can rewrite equation (15) as a single sum

$$U_{\text{el-ion}} = \sum_{\Delta G} \sum_c e^{-i\Delta G\cdot R_i} \Omega(\Delta G) \quad (16)$$

where the kernel Ω requires the convolution of $\phi_c(G) c_{nk}(G)$ with its complex conjugate, a computation which can be completed in $\mathcal{O}(N_a \log_2 N_a)$ steps using the fast Fourier transform. Thus the evaluation of the energy and its gradients for all sites can be accomplished in $\mathcal{O}(N_a^2 \log_2 N_a)$ steps. This is a significant advance since it leaves the wavefunction orthogonalization operation as the only remaining N_a^3 scaling operation in plane wave based electronic structure calculations [1].

However, in addition to its computational efficiency, a significant advantage of the reciprocity rule is that it relates the forces seen by the ions to the spatial distribution of the electronic charge density in a direct and physically transparent way. This is likely to be extremely useful for interpreting atomic relaxations near surfaces and defects in solids, for which the relaxations can be quite complicated, but which are nonetheless determined by the spatial redistribution of the valence electron density. In principle one might be able to exploit the composition of the nonlocal potential in equation (15) to clearly isolate contributions to the force due to the s- p- and d-like components of the charge density.

In summary, by exploiting a reciprocity relation for the electron-ion interaction one may reformulate the problem of calculating atomic forces in electronic structure codes into a single computation which will simultaneously yield the force distribution at all lattice sites in the system. The method scales efficiently with system size and directly relates the computed forces to the spatial distribution of the electronic charge density.

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[7] This also differs from the $\mathcal{O}(N_a^2)$ method of reference [3] which is carried out in real space; our algorithm is carried out completely in reciprocal space, and is especially well suited for plane wave based electronic structure methods.
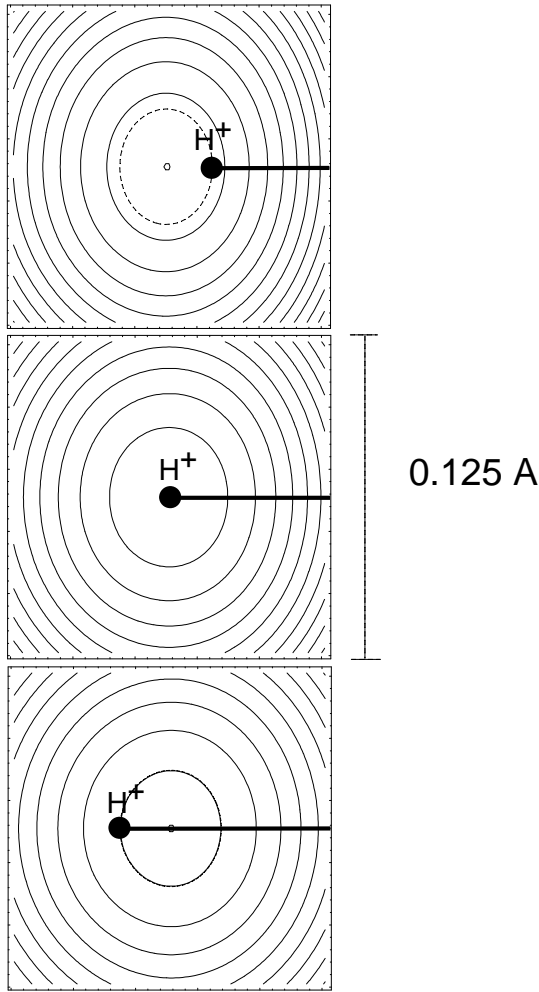
0.125 A

FIG. 1. Contour plots of the effective potential of equation (6) seen by an H^+ ion in H_2 calculated at bond lengths of 0.70A (top), 0.78A (equilibrium, middle) and 0.90A (bottom). The equipotentials are equally spaced at intervals of 50 meV. The location of the H^+ ion is given by the bold dot. The string running off each panel to the right terminates on the other H^+ ion.
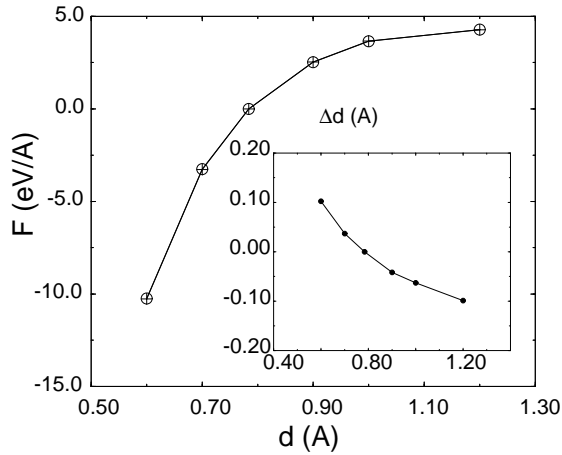
FIG. 2. The force on an H^+ ion in H_2 calculated using the full Coulomb potential plotted as a function of interatomic separation. The plot overlays the results from the Hellmann-Feynman force theorem (open circles) and the force obtained from the reciprocity relation discussed in the text (crosses). Here a positive force represents an attractive force. The vertical axis of the inner panel gives the offset between the interatomic separation and the distance between potential minima calculated for each interatomic separation.
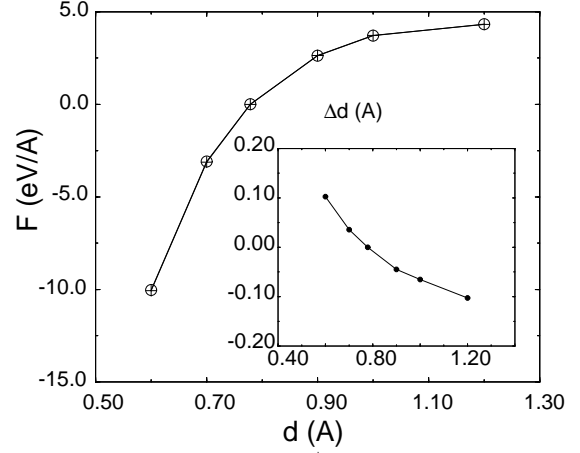

FIG. 3. The force on an H^+ ion in H_2 calculated using a local pseudopotential plotted as a function of interatomic separation. The plotting conventions are the same as those of figure (2).
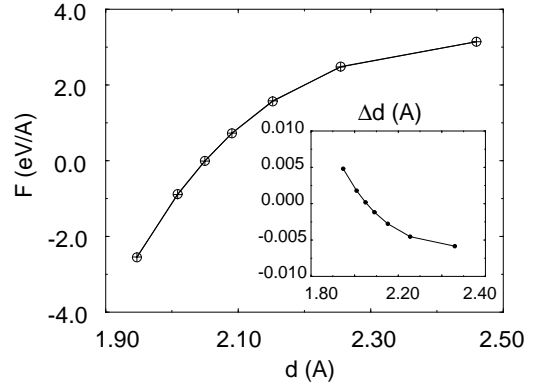

FIG. 4. The force on a Cl ion in Cl_2 calculated using a nonlocal pseudopotential plotted as a function of interatomic separation. The plotting conventions are the same as those of figure (2).

4